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The metastable growth of diamond films has been achieved by a number of continuous plasma-enhanced chemical vapor deposition (CVD) methods. Of these, none have gained more attention than the CW microwave plasma-enhanced chemical vapor deposition technique ~~[1].~~ In this technique the amount of microwave power used is typically limited by the extent of substrate heating induced by plasma and microwave heating. Concomitantly, the restriction in the amount of microwave power that can be used also reduces the amount of reactants that are dissociated and hence the film's growth rate.

The use of pulsed radio-frequency discharges of very high power to deposit thin films has recently been reported by Scarsbrook ~~et al [2].~~ In this paper we investigate the use of microwave induced pulsed plasmas in the growth of diamond films.

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# Synthesis of Diamond Films By Microwave Generated Pulsed Plasmas

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**Introduction** - The metastable growth of diamond films has been achieved by a number of continuous plasma-enhanced chemical vapor deposition (CVD) methods. Of these, none have gained more attention than the CW microwave plasma-enhanced chemical vapor deposition technique [1]. In this technique the amount of microwave power used is typically limited by the extent of substrate heating induced by plasma and microwave heating. Concomitantly, the restriction in the amount of microwave power that can be used also reduces the amount of reactants that are dissociated and hence the film's growth rate.

The use of pulsed radio-frequency discharges of very high power to deposit thin films has recently been reported by Scarsbrook et al [2]. In this paper we investigate the use of microwave induced pulsed plasmas in the growth of diamond films.

**Experimental Procedure** - A microwave plasma-enhanced chemical vapor deposition system with a dielectric waveguide was used in the deposition of the diamond films. The operation of this system has been described previously [3]. The microwave transmitter was modified to include a Phillips PM5715 pulse generator for pulse operation, and the maximum power output was increased to 2.5KW at 7.36 +/- 0.050 GHz.

Depositions were performed on (100) silicon n-type substrates. To aid in the nucleation and reduce the time necessary to nucleate the diamond film the substrates were seeded by abrading them with diamond crystals that were up to 2 micrometers in size. The silicon substrates were placed horizontally on sapphire tiles that rested on the inner chamber just above the output end of the dielectric waveguide. This procedure was used to minimize the potential contamination of the diamond deposit with silica from the dielectric waveguide.

Depositions were performed at 5 torr, with and without the use of external heating. When a furnace was not used the substrate was heated only by the plasma and microwave heating. Substrate temperatures were measured with a Chapin Tec, Model ROS-5U two color optical pyrometer. In part, because of limited access in viewing the substrate only a deposition temperature range of between 800 and 1050$^{\circ}$C could be determined.

The gas flow rates during deposition were 50 cc/min argon, 100 cc/min hydrogen, 0.5 cc/min oxygen, and 0.5 cc/min methane. Deposition times ranged between 7 and 8 hours. The average deposition rate of the film was obtained from the thickness and the total time of deposit.

**Results and Discussion** - Pulsed plasmas were run in the nanosecond, microsecond, and millisecond ranges. The system was set to obtain the system's peak power for all pulsed plasma depositions. Duty cycles were set to obtain an average power that were similar to the power used in the CW baseline depositions.

In the nanosecond range, with a pulse duration and repetition time of 54 and 100 nanoseconds respectively, the deposited film was not continuous. An SEM micrograph of the discrete crystallites are shown in Figure 1a.

Increasing the pulse duration and repetition time to 5 and 10 microseconds respectively, the deposited film exhibited mostly (111) faceting as can be seen in Figure 1b. Facets, primarily the (111) were typically submicrometer in size. However, some of the (100) facets were found to be 2.5 micrometers in length. The film's deposition rate was 0.4 micrometers per hour.

In the millisecond pulsed-plasma range, with a 5.6 millisecond pulse duration and a 10 millisecond repetition time, the film exhibited both (111) and (100) faceting with the (111) facets still predominating. An SEM micrograph is shown in Figure 1c. The largest (100) facet faces measured 5 micrometers in length. The film's deposition rate was 0.8 micrometers per hour.

For comparison purposes a baseline CW plasma was deposited. The SEM micrograph of this film is shown in Figure 1d. As can be seen, both the (100) and (111) facets are present. The largest (100) facets measured 12 micrometers in length. The film's deposition rate was 1.5 micrometers per hour.

A Rigaku Rotaflex RU 200B X-ray diffractometer was used to obtain an X-ray diffraction pattern of the millisecond range pulsed plasma film. The x-ray diffraction pattern of the 6 micrometer film is shown in Figure 2. Stick figures of the standard powder pattern of natural cubic diamond defining the location and intensity are also shown. The sharp peaks not located at the stick figures are that of the crystalline (100) oriented silicon substrate. Of particular interest is the deviation between the standard powder pattern stick figures relative intensity ratios and that of the intensity rations of the deposited diamond films. These differences indicated that the deposited diamond film crystal orientation is non-random and exhibits a preferred texture.

Micro-Raman spectra of the millisec pulsed deposited film and the baseline CW plasma deposited film was generated by Instruments SA on their Raman Microprobe S3000 spectrophotometer and are shown in Figure 3. The msec pulse film shows a broad diamond peak about 1332.4 $cm^{-1}$ and a broad non-diamond peak about 1500 $cm^{-1}$. By comparison, the Raman spectrum of the baseline CW plasma deposited film exhibited a sharp diamond peak with a full width at half maximum (FWHM) of 5.5 $cm^{-1}$, at 1333.6 $cm^{-1}$ and with no other carbon peaks present.

Although the pulsed plasma average power levels were similar to those used in the CW plasma baseline, the use of pulsed plasmas can result in reduced heating of the substrate. Since the deposition rate of diamond is temperature dependent, additional substrate heating was provided by heating the substrates to 600$^{\circ}$C before the plasma was ignited. A minor improvement in film thickness indicated that the growth temperature could have been optimized for maximum growth.

The thickness of the deposited films by the pulsed plasma technique increased with the pulse width. This would indicate that the generation rate of the active species was less for shorter pulse widths and that its recombination rate was not significantly affected by the longer millisec off periods. With pulse rise times on the order of a few nanoseconds the explanation may lie with the time it takes for the active species, within the plasma to reach maximum concentration.

As with CW plasmas, the size of the diamond crystallites deposited with pulsed plasmas did increase with film thickness. From the SEM micrographs the pulsed plasma deposited crystal facets appeared to be well formed. The micro-Raman spectra indicated the quality of the diamond film deposited by the millisec pulsed plasma is less than that of the CW plasma deposited film. This result can not be attributed to its crystal size. For the experimental conditions used, one possible explanation is that the active species which contribute to sp3 diamond carbon formation recombine during the pulse off time and are significantly reduced during this portion of the deposition cycle.

**Summary** - Diamond films were deposited under pulsed-plasma conditions. The quality and film thickness were dependent on the pulse conditions. It was found that the film thickness increased with pulse duration and repetition time, and that their quality may be a function of the length of time that the pulse is off.

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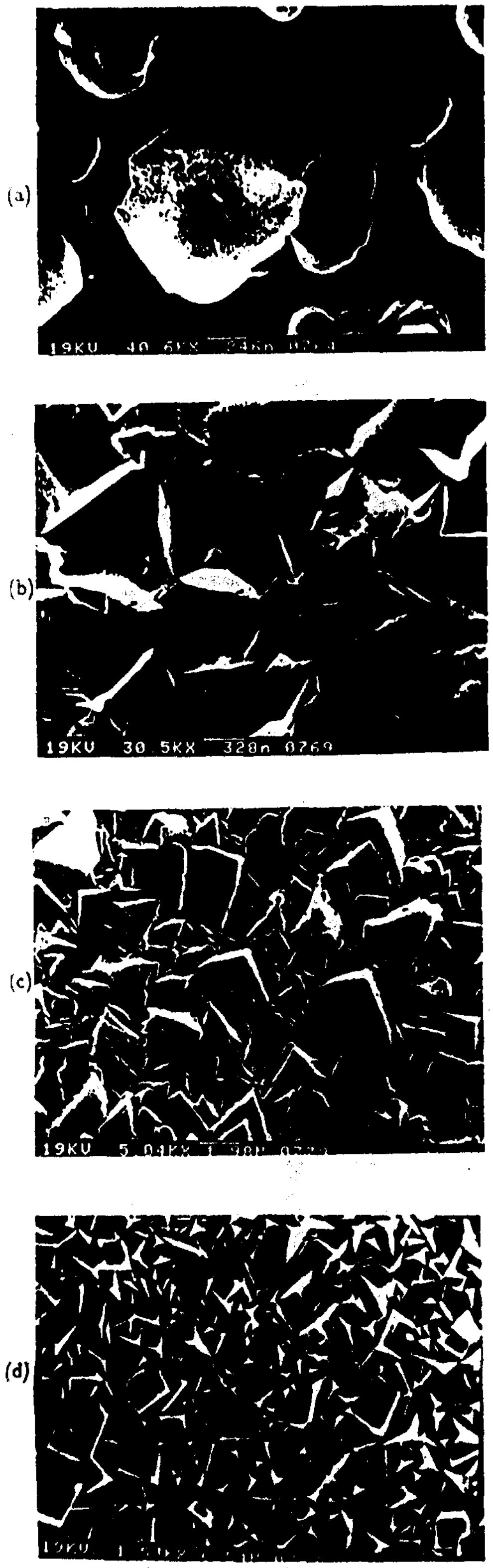


Figure 1. SEM microphotographs of deposited diar films. (a) nanosec pulsed plasma; (b) microsec p plasma; (c) millisec pulsed plasma; and (d) CW plas

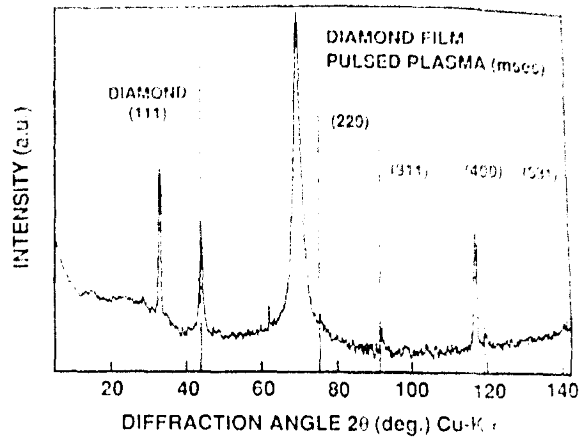


Figure 2. XRD pattern of millisec pulsed deposited diamond film.

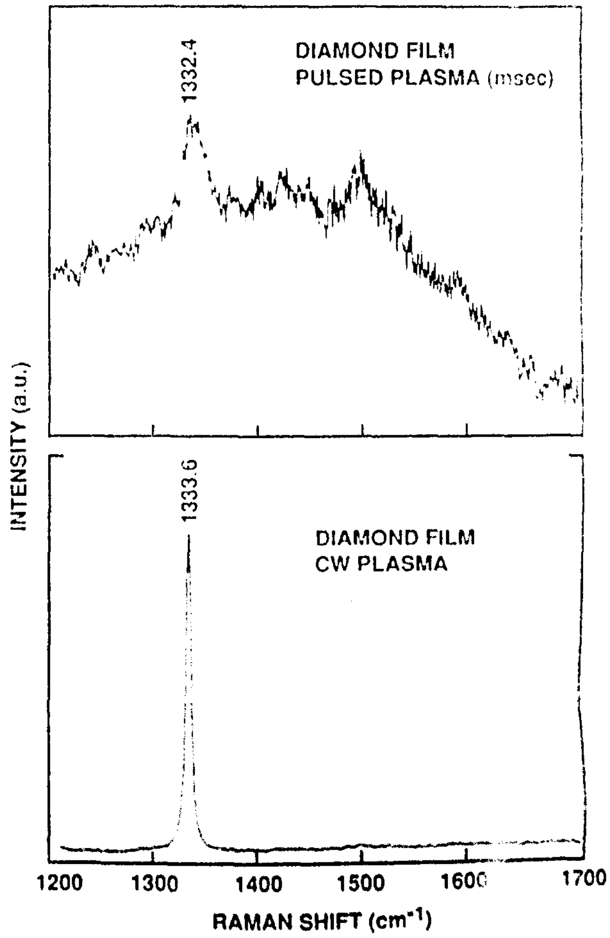


Figure 3. Micro-Raman spectra of millisec pulsed deposited diamond film and CW plasma baseline deposited film.